

Torbjörn Jacobson

Polyquinanes

Studies on the Synthesis of Compounds
Containing Accumulated Pitzer Strain

Lund 1973

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This publication is a thesis for the degree of doctor of philosophy at the University of Lund. It is a summary of the following papers, all written by one author (I. T. J.):

1. Polyquinanes. A Simple Synthesis of Tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene. Acta Chem. Scand. 21, 2235 (1967).
2. Polyquinanes II. Further Studies on the Chlorination of all-cis-Tricyclo[5.2.1.0^{4,10}]decane. Acta Chem. Scand. 26, 2477 (1972).
3. Polyquinanes III. Dechlorination of Chlorinated Derivatives of Triquinacene. Chem. Scripta 2, 121 (1972).
4. Polyquinanes IV. Conformational, Stereochemical and Preparative Aspects of the Insertion Reaction of 10-Carbenabicyclo[5.2.1]decane. Chem. Scripta 2, 127 (1972).
5. Polyquinanes V. 1,2,3,5,6,8,9-Heptachloro-all-cis-tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene. Chem. Scripta, accepted for publication.
6. Polyquinanes VI. Structures and Chemistry of Dimeric Compounds Derived from Chlorinated Derivatives of Tricyclo[5.2.1.0^{4,10}]deca-1(10),2,5,8-tetraene. Part A: Primary Dimers. Chem. Scripta, accepted for publication.
7. Polyquinanes VII. Structures and Chemistry of Dimeric Compounds Derived from Chlorinated Derivatives of Tricyclo[5.2.1.0^{4,10}]deca-1(10),2,5,8-tetraene. Part B: Simple Transformations of Primary Dimers. Chem. Scripta, accepted for publication.
8. Polyquinanes VIII. Dilithium Hexachloroacepentylenediide, a Stable Species in Solution at - 70°. Chem. Scripta, accepted for publication.

These papers will be referred to as Ref. 1, 2 ... 8, below.

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Abstract. The polyquinanes form a class of fused five-membered ring compounds of theoretical importance. A definition of the polyquinane concept based upon graph theory is given. The properties expected for the higher, so far unknown members in the polyquinane series are briefly discussed. It is found that for certain of these compounds the total strain-energy is likely to rise steeply upon any appreciable distortion from a conformation in which the Pitzer strain energy is close to the maximum possible for the number of ethanoid fragments present, and the bond-angle strain energy is close to zero. (Small distortions away from the perfectly eclipsed conformation may, however, possibly lower the total strain energy somewhat in some of the cases of interest.) This makes the members in question attractive objects for a variety of investigations of theoretical interest. Syntheses and investigations of polyquinanes so far made are reviewed, with particular emphasis on derivatives of tricyclo[5.2.1.0^{4,10}]decane.

1. Introduction

The purpose of part of the research carried out in the author's laboratory during the last few years¹⁻⁸ has been to find a simple high yield entry of some degree of generality into the polyquinane series of compounds (to be defined in section 2, below). Of particular interest was the problem of the synthesis of dodecahedrane, the upper limiting member of the polyquinane series and a compound of great theoretical interest (cf. section 3.5). Work has also been directed toward the synthesis of this hydrocarbon in other laboratories^{49,51,73}. If a convenient synthesis of dodecahedrane could be found, certain other higher members of the polyquinane series could probably also be easily prepared by degradations of dodecahedrane. The simplest way that may be visualized to yield dodecahedrane would be by the thermally symmetry-forbidden⁹ process I $\rightarrow$ II, a process which has so far not been possible to realize experimentally (cf. section 4.2.5)*. However, if

* The simple structural relationship between the structure

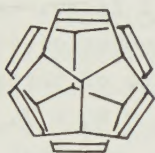
now called triquinacene (i.e. one of the molecules in formula I) and dodecahedrane, as expressed in the transformation I $\rightarrow$ II, was realized by the present author in September 1958 and was e.g. demonstrated by him to Dr. L. Eberson and Dr. J. Sandström at the University of Lund in May 1963. The same relationship has been found by professor R.B. Woodward, Harvard University, and was published by him in August 1964⁴⁹. Since the same idea has occurred independently to two different persons in a span of a few years, it would seem that neither person can claim the exclusive priority of the idea; cf. Ref. 53, footnote 2. It should be added that a claim such as that in Ref. 53, footnote 2, would hardly have been made by professor Woodward himself, since he knew by way of private contacts from an early stage (December 1965) about the present author's independent ideas and research.

That the research carried out on the structures I and II by the present author was started independently is also mentioned in Ref. 1 in a footnote (p. 2236).

the process I $\rightarrow$ II actually turns out to be essentially impossible to realize, an immense number of variations of the same basic idea of skeletal build-up* are still available, in which the tricyclic reactants have been modified with respect to the nature of the substituents and the degree and pattern of the unsaturation, and which still have the merit over most other approaches of a potential feasibility of a very simple build-up of the dodecahedrane carbon skeleton. Crucial for the simplicity of the approach will be easy access to desired derivatives of tricyclo[5.2.1.0^{4,10}]decane. Such derivatives are of substantial interest also for the build-up of polyquinanes containing only one or a few five-membered rings more than tricyclo[5.2.1.0^{4,10}]decane itself. Furthermore tricyclo-

* By the basic idea should be understood that the carbon skeleton of dodecahedrane is derived from two pre-formed tricyclo[5.2.1.0^{4,10}]decane carbon skeletons united by six single bonds in one or more steps.

[5.2.1.0^{4,10}]decane and certain of its derivatives are of substantial theoretical interest as such (cf. sections 3 and 4.2).



I



II

For these reasons the studies by the present author in the polyquinane field have so far been entirely confined to the chemistry of tricyclo[5.2.1.0^{4,10}]decane and its derivatives, in particular such aspects of this chemistry that could be potentially useful in a synthesis of dodecahedrane. Research on the chemistry of tricyclo[5.2.1.0^{4,10}]decane has also been carried out in several other laboratories during the last few years (cf. section 4.2). The effect of the combined effort of the several investigators working in the field is that a representative collection of important derivatives of the system are now known and that a familiarity with the unusual properties of this system has begun to emerge. Recently some most interesting results from other sections of polyquinane chemistry have also appeared from other laboratories (cf. section 4.3).

The purpose of the present review, aside from giving a definition of the polyquinane concept and a theoretical background of some of the studies in the polyquinane field, is to summarize work so far carried out in this field. Emphasis will of necessity be on derivatives of tricyclo[5.2.1.0^{4,10}]decane, as a consequence of the present status of knowledge. The literature has been covered as far as possible to December 1972.

2. Definition of the Polyquinane Concept

Consider the set M of planar¹⁰, regular¹⁰ (vertices of order ρ) graphs with the property that two faces of a graph have never more than one edge (and two vertices) in common, and with the property that in a graph all faces, except possibly the infinity face¹⁰, have the same number of edges ρ^* . It may easily be demonstrated that M consists of three subsets, M_1 , M_2 , and M_3 | $M_i \subset M$, $i = 1, 2, 3$; $M_i \cap M_j = \emptyset$, $i \neq j$, $M_1 \cup M_2 \cup M_3 \supseteq M$, with unique properties, and that a graph always may be assigned to either M_1 , M_2 , or M_3 depending upon the value of the function

$$F = \frac{\rho}{2} - \frac{\rho}{\rho^*}$$

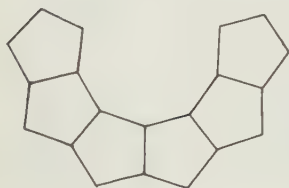
so that {every graph with $F < 1$ } $\in M_1$, {every graph with $F = 1$ } $\in M_2$, and {every graph with $F > 1$ } $\in M_3$. The easiest way to realize this seems to be to identify M with a set of networks isomorphic with M in which the edges consist of rigid rods of equal length and in which all of the faces are regular polygons*. Under these circumstances F means the sum of the ρ corner-angles that meet at a vertex in the interior of a network, in radians divided by 2π .

It is obvious that in order to obtain a convex network which may be built up to a regular polyhedron, $F < 1$ is a necessary condition. It is, however, not a sufficient condition, because the set isomorphic with M will also contain bandlike (often helicene-like in chemical language) structures such as e.g. those shown in formulae III and IV. These structures can never be built up into a regular polyhedral structure by the addition of new rings. When $F = 1$ a set (isomorphic with M_2) is obtained which contains (among other structures) planar, helicene-fragment-free networks such that surfaces of arbitrary shape and arbitrarily large are (area

* Properly speaking this set of networks is isomorphic with a subset of M only, because several members of M_3 are physically impossible to construct with faces which are regular polygons (cf below). This is of little importance for the

discussion to be given below, however.

expressed in l^2 , l = length of the rigid rods) may be covered, i.e. unlimited growth of the planar, helicene-fragment-free network in all directions is possible. When $F > 1$ unlimited growth in all directions of a similar network is physically impossible, due to overcrowding at the periphery of the network. (Band and tree like structures may, however, still grow out to unlimited dimensions.)



III



IV

Due to the isomorphism between the set of structures just considered and M , the results just obtained may be reformulated so as to apply to M . It is thus, e.g., obvious that M_1 and only M_1 (besides band- and helicene-like graphs) contains graphs which may be built up into upper limiting members with the property that the infinity face has the same number of edges as the other faces. However, since no corner-angles or even shapes of edges are fixed in the general case of the graphs belonging to M , it is also apparent that a different derivation of the relationships involving F based upon the combinatoric properties of the graphs must be possible and preferable. A simple combinatoric derivation of an inequality equivalent to that of $F < 1$ (i.e. formula 8.4.3 in Ref. 10), and a demonstration that fulfillment of this inequality is a necessary condition for a graph with the same number of edges in all faces (including the infinity face) to be possible, may be found in Ref. 10. A combinatoric derivation of a relation-



$$\begin{aligned} p^* &= 3 \\ p &= 7 \\ F &> 1 \end{aligned}$$



$$\begin{aligned} p^* &= 3 \\ p &= 6 \\ F &= 1 \end{aligned}$$



$$\begin{aligned} p^* &= 3 \\ p &= 5 \\ F &< 1 \end{aligned}$$



$$\begin{aligned} p^* &= 3 \\ p &= 4 \\ F &< 1 \end{aligned}$$



$$\begin{aligned} p^* &= 3 \\ p &= 3 \\ F &< 1 \end{aligned}$$



$$\begin{aligned} p^* &= 4 \\ p &= 6 \\ F &> 1 \end{aligned}$$



$$\begin{aligned} p^* &= 4 \\ p &= 5 \\ F &> 1 \end{aligned}$$



$$\begin{aligned} p^* &= 4 \\ p &= 4 \\ F &= 1 \end{aligned}$$



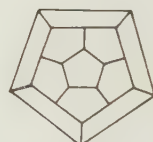
$$\begin{aligned} p^* &= 4 \\ p &= 3 \\ F &< 1 \end{aligned}$$



$$\begin{aligned} p^* &= 5 \\ p &= 5 \\ F &> 1 \end{aligned}$$



$$\begin{aligned} p^* &= 5 \\ p &= 4 \\ F &> 1 \end{aligned}$$



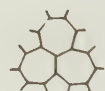
$$\begin{aligned} p^* &= 5 \\ p &= 3 \\ F &< 1 \end{aligned}$$



$$\begin{aligned} p^* &= 6 \\ p &= 6 \\ F &> 1 \end{aligned}$$



$$\begin{aligned} p^* &= 6 \\ p &= 3 \\ F &= 1 \end{aligned}$$



$$\begin{aligned} p^* &= 7 \\ p &= 3 \\ F &> 1 \end{aligned}$$

Scheme I.

ship equivalent to $F = 1$ and a demonstration that fulfillment of this kind of relationship is a necessary requirement for a planar, nonhelicene-like infinitely large graph to be possible may also be found in Ref. 10 (pp. 106-108). (A more indepth coverage of certain aspects of the above graphs may be found in Ref. 11 and 12. For recent progress in the field of convex polytopes, see also Ref. 13.) The shapes of networks containing no band- or helicene-like fragments for representative values of ρ and ρ^* are shown in Scheme I.

The above considerations have some interest for chemistry. The cases $\rho = 4$, $\rho^* = 3$ and $\rho = 5$, $\rho^* = 3$ thus obviously apply to boron chemistry¹⁴, whereas cases with $\rho = 3$ apply to carbon chemistry. For the case $\rho = 3$, $\rho^* = 6$ we will thus define a series of hydrocarbons, the perihydrographites, as follows:

Every member of the series should be derivable from other, more simple members of the series and finally from the parent six-membered cycloalkane, $(CH_2)_m$ by successive substitutions of hydrogens by $(CH_2)_n$ -fragments, $n = 0, 1, 2 \dots (m-2)$. [$n = 0$ means that two methylene groups in the more simple hydrocarbon are directly united by a bond.] The substitutions are performed so that

1. new rings always will be six-membered,
2. every ring in the ring-system will have two carbon atoms in common with every adjacent ring,
3. only creation of hydrocarbons of the constitution $(CH)_j(CH_2)_k$ is allowed, and
4. uniting a new $(CH_2)_n$ fragment with a carbon atom in a methylene group of a ring system is never allowed when (after a suitable choice of the stereochemistry of the ring system) a direct union of this carbon atom by a bond with another methylene carbon atom already belonging to the ring system is possible and leads to the formation either of another six-membered ring, or of such a ring with more than six carbon atoms that a $(CH)_r$, $r = 0, 1, 2 \dots$, fragment^{*} exists whose

* The carbon atoms of the fragment may all be connected with each other by bonds or the fragment may consist of two or

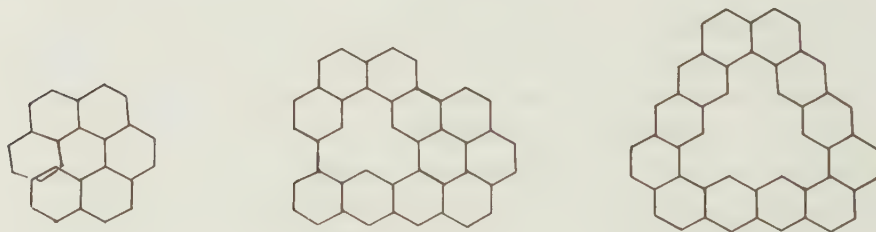
more separate parts $(CH)_s$ in which this is so. Bonds created directly between methylene groups in the more-than-six-membered ring are assumed to belong to the fragment.

number of free valences is equal to the number of methylene groups in the large ring considered and which upon suitable combination with these methylene groups divides the surface surrounded by the more-than-six-membered ring into a regular pattern of six-membered rings. (This possibility to form rather strain-free, more-than-six-membered rings under suitable circumstances may not be utilized in the build-up of higher members in the series of hydrocarbons just defined. This would violate condition 1. above.)

Examples of hydrocarbon structures belonging to and not belonging to the perhydrographite series are shown in Schemes II and III, respectively.



Scheme II. Examples of hydrocarbon structures which belong to the perhydrographite series according to the definition given in the text.



Scheme III. Examples of hydrocarbon structures which do not belong to the perhydrographite series.

If the above considerations are transferred to polycarbocyclic structures corresponding to graphs with $\rho = 3$ and $\rho^* = 3, 4, 5$, or, e.g. 7, in such a way that in the above definition "six" and "six-membered" is everywhere exchanged for "three" and "three-membered", for "four" and "four-membered", etc.^{*}, whereas the other conditions are kept unchanged, most interesting series of structures are obtained. The three-, four- and five-membered ring series of compounds defined in this manner will be called polytertianes, polyquartanes, and polyquinanes below.

The polytertiane, polyquartane, and polyquinane series all contain only a limited number of members, thus contrasting with the perhydrographite series. (This state of affairs is a consequence among other things of condition 4. above, which prevents formation of band- and helicene-like structures.) The carbon skeletons of the upper limiting members in the three series may be represented by the networks shown to the right in Scheme I for $\rho = 3$ and $\rho^* = 3, 4$ and 5. All other members in these series may be thought to arise by removing parts of these upper limiting ring systems with saturation of arising free valences with hydrogen.

The upper limiting member in the polytertiane series, tetrahedrane, is not known and presumably too labile to be synthesized¹⁵. The upper limiting member in the polyquartane series, cubane, on the other hand, is well investigated¹⁶ and rather stable. The number of lower members in the two series is, furthermore, small (2 and 5, respectively, aside from stereoisomers) and the more important of these members are already known¹⁷⁻¹⁹, so that the possibilities of further preparative progress in these series seem rather limited.

In the polyquinane series (cf. Scheme IV), on the other hand, much still remains to be done and reasons may also be given both why it is justified to consider this series as a special class of compounds that may be given a name (cf. below), and why investigations of the series are of some interest (cf. section 3). However, before this is done some further, auxiliary definitions will be introduced in order to simplify the discussion. It is seen that of the structures in Scheme IV,

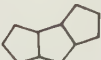
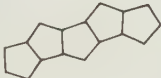
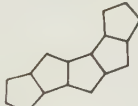
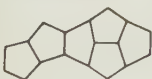
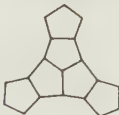
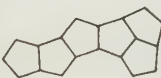
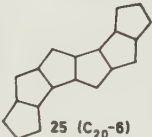
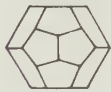
* In the three-membered ring case, condition 4. above is unnecessary.

those with the numbers 3, 5, 9, 15, 16, 17, 26, 27, 32, 33, 35, 36, 37, 38, and 39 are unusual, in so far as fusions are present but isolated ortho-fusions are absent. For this reason the stereochemistry of any of these ring systems is completely described by a prefix such as all-cis, i.e. additional syn anti stereoisomerism will not be possible. Indeed it is doubtful whether the preparation of anything but the all-cis-isomers will ever be possible for any of these ring systems, because other stereoisomers would be excessively strained, in particular in the case of higher members of the series. These ring systems will be called "unconstricted polyquinanes" (or "unconstricted all-cis-polyquinanes" when specification of stereochemistry is desired). In the other fused ring systems of Scheme IV, isolated ortho-fusions are present, and syn anti isomers are possible (except in 2). Taking these facts into account, the prefix acs will be introduced. When used in the combinations acs-polyquinanes, acs-stereoisomers and acs-stereochemistry, it means that all of the unconstricted all-cis-polyquinanes, the all-cis, all-syn-polyquinanes, 1 and cis-2, are considered.

Several reasons may be given why it is justified to consider the polyquinanes as a special class of compounds that may be given a name. A few of these reasons will now be summarized.

1. The number of members in the polyquinane series is limited, but sufficiently large that a class-name is justified. The number of members is 39, aside from stereoisomers; cf. Scheme IV.

2. The greatest similarities between different members in the polyquinane series are expected to be observed if only members with acs-stereochemistry are considered. However, the general class of polyquinanes is also expected to show many unique properties. This is intimately related to the fact that cis-bicyclo[3.3.0]octane is less strained than trans-bicyclo[3.3.0]octane (see section 4.1.2) and that all-cis-tricyclo[5.2.1.0^{4,10}]decane is certainly less strained than any other stereoisomer of tricyclo[5.2.1.0^{4,10}]decane (cf. section 4.2.3), which will have a variety of consequences for the courses of

				
1 (C ₅ -1)	2 (C ₈ -2)	3 (C ₁₀ -3)	4 (C ₁₁ -3)	5 (C ₁₂ -4)
				
6 (C ₁₃ -4)	7 (C ₁₄ -4)	8 (C ₁₄ -4)	9 (C ₁₄ -5)	10 (C ₁₅ -5)
				
11 (C ₁₆ -5)	12 (C ₁₆ -5)	13 (C ₁₇ -5)	14 (C ₁₇ -5)	15 (C ₁₅ -6)
				
16 (C ₁₆ -6)	17 (C ₁₆ -6)	18 (C ₁₇ -6)	19 (C ₁₈ -6)	20 (C ₁₈ -6)
				
21 (C ₁₈ -6)	22 (C ₁₉ -6)	23 (C ₁₉ -6)	24 (C ₁₉ -6)	25 (C ₂₀ -6)
				
26 (C ₁₇ -7)	27 (C ₁₈ -7)	28 (C ₁₉ -7)	29 (C ₁₉ -7)	30 (C ₂₀ -7)
				
31 (C ₂₀ -7)	32 (C ₁₈ -8)	33 (C ₁₉ -8)	34 (C ₂₀ -8)	35 (C ₂₀ -8)
				
36 (C ₁₉ -9)	37 (C ₂₀ -9)	38 (C ₂₀ -10)	39 (C ₂₀ -11)	

Scheme IV. The Polyquinanes. Under each formula the number of carbon atoms (k) and the degree of cyclization (l) has been indicated as " C_k-l ".

chemical reactions in the general polyquinane series.

3. The chemical properties of acs-polyquinanes and their derivatives are expected to show many similarities and often to be appreciably different from properties observed e.g. for representatives of the perhydrographite series. Thus substitution reactions at bridgeheads are often likely to occur with complete retention of configuration. The likelihood will be greatest in the case of the unconstricted all-cis-polyquinanes (cf. e.g. the second paragraph of section 4.2.4) and at bridgeheads that belong to peri-fusions in the case of the other polyquinanes. Elimination reactions involving two adjacent bridgeheads will probably be possible for the most part, but will often lead to the formation of a highly reactive tetraalkyl substituted double bond which is prone to undergo addition reactions with reformation of a more saturated polyquinane system with acs-stereochemistry. (Cf. e.g. the properties of perchloro-cis-tricyclo[5.2.1.0^{4,10}]deca-1(10),2,5,8-tetraene described in section 4.2.7.) This is markedly different from elimination reactions in the perhydrographite series, since products of the latter reactions containing a tetraalkyl substituted double bond will mostly be quite inert to additions at that double bond. Bridgehead reactivities, as measured by solvolysis rates, are likely to often be unusual and not easily predictable on the basis of presently available theories developed from measurements on other classes of compounds (cf. section 4.2.9). acs-Polyquinanes are, furthermore, e.g. likely to all be thermally quite stable.

4. The physical properties of several of the higher acs-polyquinanes, notably the unconstricted ones, are expected to show similarities, because the gross outer shape of any of the corresponding molecules will be that of a sphere of the same diameter.

5. A variety of synthetic transformations between polyquinanes should be possible. Viewed in this perspective Scheme IV may be seen as a collection of structures containing a few objects of unusual interest as such, in particular 3, 5, 15, and 39 (cf. section 3) and many more skeletal structures of potential

intermediates for the synthesis of these objects.

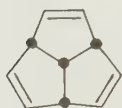
Before terminating the present section a few additional, general comments on the properties of the collection of structures shown in Scheme IV will be made. It can be seen from the Scheme that the number of structures for the degrees of cyclization 1, 2, 3 ... 11 are 1, 1, 2, 4, 6, 11, 6, 4, 2, 1, and 1. This symmetry of the polyquinane series is due to the fact that for each member of the series, p , there exists another ring system, $\bar{p}$, which is also a member of the series and which has the property that when fused together with p it will yield the completed dodecahedron*. If the ring systems are numbered as in Scheme IV, p and $\bar{p}$ are related to each other as follows ($p, \bar{p}$): (1,39), (2,38), (3,36), (4,37), (5,32), (6,33), (7,34), (8,35), (9,26), (10,27), (11,28), (12,29), (13,30), (14,31), (15,15), (16,16), (17,17), (18,18), (19,20), (20,19), (21,21), (22,22), (23,23), (24,24), (25,25), (26,9), (27,10), (28,11), (29,12), (30,13), (31,14), (32,5), (33,6), (34,7), (35,8), (36,3), (37,4), (38,2), and (39,1).

Of the different dodecahedral circuits corresponding to the peripheral contours of the ring systems in Scheme IV, that of system 25 is unique, since it is, of course, the only circuit which is also a Hamiltonian line of the dodecahedron.

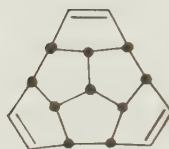
Further structures of special interest in Scheme IV are those numbered 3, 16, 19 and 39. These are the structures from which $(CH)_n$ hydrocarbons may be derived (after introduction of unsaturation, when necessary). These hydrocarbons should be interconvertible with other $(CH)_n$ hydrocarbons by methods now under rapid development in the expanding field of $(CH)_n$ hydrocarbon chemistry¹⁵. We propose that the $(CH)_n$ hydrocarbons with acs-stereochemistry derived from 3, 16, 19, and 39 be collectively called polyquinacenes and that the all-cis- and all-cis, all-syn- $(CH)_n$ -hydrocarbons derived from 16 and 19 be called C_{16} -hexaquinacene and C_{18} -hexaquinacene, respectively. These trivial names conform to the previously adopted

* Each of the pairs $(p, \bar{p}) \equiv (\bar{p}, p)$ may be identified with one cyclic arc (= circuit) of the dodecahedron; cf. Ref. 10, p. 22.

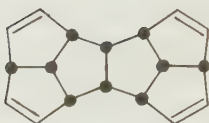
triquinacene⁴⁹. The structural formulae of the polyquinacenes are shown in Scheme V.



Triquinacene



C₁₆-Hexaquinacene



C₁₈-Hexaquinacene



Dodecahedrane

(Globan, Dodecaquinacene)

Scheme V. The Polyquinacenes.

It should be pointed out that a preparation of triquinacene involving typical (CH)_n hydrocarbon transformations has already been accomplished; see the last paragraph of section 4.2.4. A potentially feasible, typical (CH)_n hydrocarbon chemistry route to C₁₈-hexaquinacene will be proposed in section 4.3.2.

3. Theoretical Significance of the Polyquinanes

3.1 Introduction

acs-Polyquinanes of particularly great theoretical interest are those which, according to presently commonly used classical mechanical models of the strain situation in saturated hydrocarbons²⁰⁻²⁵, are expected to have conformations

of minimum total strain energy close to a perfectly eclipsed conformation, in which bond angles are close to ideal tetrahedral angles. This conformation will be designated the PE conformation below and will be defined geometrically in section 3.2. Also, what is meant by the expression that two conformations are close to each other must be defined (section 3.3) before the discussion is continued. Then acs-polyquinanes of theoretical interest will be sorted out and discussed briefly from theoretical points of view (sections 3.4 and 3.5).

3.2 Geometrical Definition of the PE Conformation

By the PE conformation of an acs-polyquinane molecule should be understood the arrangement of atoms in space that arises when a suitable fragment is cut out of a dodecahedrane molecule with a regular dodecahedral arrangement of its carbon nuclei, without changing the coordinate interrelationships of the carbon nuclei of the fragment and with saturation of arising free valences with hydrogen. The skeletal structure of the fragment should, of course, be that of the acs-polyquinane molecule considered. C-H bonds of the resulting structure will be of two kinds, i.e. out-pointing and in-surface. In the PE conformation the out-pointing C-H bonds should all fulfill the requirement that the hydrogen nucleus belonging to a bond should be situated on the line of connection between the symmetry centre of the (completed) regular dodecahedral carbon framework and the adjacent carbon nucleus*. The in-surface C-H bonds should all fulfill the requirement that the line of connection between the carbon and hydrogen nuclei belonging to a bond should coincide with a line of connection between two adjacent carbon nuclei in the corresponding completed regular dodecahedral framework*.

* The somewhat special arrangement of the methylene hydrogens in the PE conformation has been chosen in order to make calculations in section 3.4 as simple as possible. It will be obvious in sections 3.4 and 3.5 that a variation of the hydrogen nuclear coordinates so as to obtain minimum total

strain energy for the carbon nuclear coordinates chosen would give hydrogen nuclear coordinates only slightly different from those chosen in all systems of interest, i.e. 2, 3, 5, 15, and 39 in Scheme IV.

Finally, in the PE conformation all C-H bond lengths should be equal. The magnitudes of the C-C and C-H internuclear distances of the PE conformation will not be stated explicitly, but these distances are assumed to be such as to give the PE conformation of dodecahedrane itself the lowest possible energy. This means that the C-C internuclear distance will probably be somewhat greater than the diamond internuclear distance, since this is typical of eclipsed ethanoid fragments (cf. e.g. C-C internuclear distances of eclipsed ethanoid fragments reported in Ref. 26 and 55). In explicit geometrical calculations, the C-C and C-H internuclear distances will be assumed to be 1.56 and 1.09 Å.

It should be added that the PE conformation as just defined will have little physical meaning for a number of acs-polyquinanes with skeletal structures as shown in Scheme IV, due to severe interpenetration of C-H orbitals. This is, however, of little importance, since the principal use of the PE conformation below will be in the discussion of a few structures in which the conformation has a physical meaning.

3.3 Definition of Similarity between Conformations

Consider two conformations A' and A'' in which the atomic nuclei have the coordinates (x'_i, y'_i, z'_i) and (x''_i, y''_i, z''_i) , $i = 1, 2 \dots n$, where every pair of singly and doubly primed coordinates with a certain value of the index i is assumed to refer to an atom with the same number in both conformations if the atoms of the molecule are numbered in a suitable manner. The distances d_i are now defined as follows

$$d_i = \sqrt{(x'_i - x''_i)^2 + (y'_i - y''_i)^2 + (z'_i - z''_i)^2} \quad .$$

For every orientation of A' and A'' with respect to each other there will exist a number d such that $d \geq d_i$ for $i = 1, 2 \dots n$, and that $d = d_i$ for at least one value of the index i . A' and A'' are next translated and rotated with respect to each other so that d reaches its smallest possible value, $d_{\min} = D$. It will now be said that the two conformations A' and A'' are only slightly distorted with respect to each other or are close to each other when D is small (typically less than 0.05 - 0.10 Å).

3.4 Search for Theoretically Interesting acs-Polyquinanes

In order to find out which of the acs-polyquinanes may be of theoretical interest, it is useful to go through Scheme IV and sort out structures that can certainly not have conformations of minimum energy close to their PE conformations. In such a selection process the structures 7(1), 11(1), 12(1), 13(1), 14(3), 18(1), 19(2), 20(1), 21(2), 22(3), 23(2), 24(3), 25(5), 27(1), 28(2), 29(2), 30(4), 31(4), 33(1), 34(3), 35(3), 37(2), and 38(1) may first be removed. (The numbers outside the parentheses refer to Scheme IV.) These are the structures that are seco-derivatives of higher members of the polyquinane series. The number of bond fissions necessary to obtain a certain system from the most extensively fused related system has been indicated in parentheses after the number of each structure in the enumeration just given. Furthermore, the structures 4(1), 6(2), 8(2), 9(1), 10(2), 16(3), 17(2), 26(2), 32(2), and 36(3) may be sorted out. In each of these structures there will be one or more extremely short (ca 0.76 Å) H-H distances between terminal hydrogens in H-C-C-C-C-H fragments in the PE conformation. The number of such H-H distances in a molecule has been indicated within parentheses after the number of each structure.

The remaining systems are 1, 2, 3, 5, 15, and 39. Of these, cyclopentane (1) is known to be appreciably distorted away from its PE conformation in its predominant conformations (cf. e.g. Ref. 27). For the remaining systems the PE conformation is destabilized by nonbonded interactions between in-surface hydrogens present in H-C-C-C-H fragments in 2(2),

3(3), 5(4), and 15(5) but not in 39. (The numbers refer to Scheme IV; the number of interactions has again been indicated within parentheses after each formula number.) The H-H distances in question will be ca 1.85 Å, corresponding to a destabilization by ca 0.8 kcal·mol⁻¹ for each H-H pair, using the H-H nonbonded potential function given by Hendrickson²⁰. The torsional strain contribution from one ethanoid fragment of the PE conformation of either of the structures will be 3.0 kcal·mol⁻¹ using either of the potential functions proposed by Wiberg²², which means that the total torsional destabilization of the PE conformations of the acs-isomers of structures 2, 3, 5, 15, and 39 will be 27, 36, 45, 60, and 90 kcal·mol⁻¹, respectively. Total bond angle strain will be close to zero in the PE conformations of all of the systems. (A total bond angle strain of 0.96 kcal/(mol C₂₀H₂₀) is calculated for the PE conformation of dodecahedrane utilizing the C-C-C and C-C-H bending potential functions used by Hendrickson²⁰.)

Distortions of the systems away from their PE conformations may release part of the large amounts of torsional strain present in these conformations. It is reasonable to assume that these distortions (if taking place) will mainly affect bond angles, and that bond lengths remain almost the same as in the PE conformations (since potential functions for alterations of bond lengths are quite "hard"; cf. e.g. Refs. 20, 22). Since it has, furthermore, already been demonstrated that nonbonded interactions between the in-surface hydrogens of acs-isomers of 2, 3, 5, and 15 (Scheme IV) will be small in the PE conformations, and since these interactions will decrease to zero upon most of the interesting distortions away from these conformations, it follows that what will be conformations of minimum total strain may be regarded as being largely determined by an interplay between torsional strain and bond angle strain. This is fortunate, since the bond angle strain situation may be simulated quite well by carefully constructed Dreiding molecular models. It follows from studies of such models that whereas cis-2 (Scheme IV) is rather flexible, the other systems, where one or more peri-fusions

have been introduced, will be appreciably more inflexible, i.e. alterations of bond angles are more highly interdependent in these systems. It also follows that all attempts to release the torsional strain present in the PE conformations of all-cis-isomers of 3, 5, 15, and 39 (Scheme IV) by changes of dihedral angles will simultaneously affect a large number of bond angles, i.e. that attempts to release the torsional strain causes bond angle strain to rise steeply. Consequently it is by no means certain that the PE conformation (or a conformation where only the nuclear coordinates of the methylene hydrogens are noticeably different from those of the PE conformation) may not be a total strain energy minimum in the case of some of the systems 3, 5, 15, and 39. What will determine whether this is so or not in a certain system will, of course, be whether or not bond angle strain rises more rapidly than torsional strain (and nonbonded interaction between the in-surface hydrogens) decreases upon all interesting kinds of alterations in the nuclear coordinates away from those of the PE conformation. (This is true provided the classical mechanical model of Ref. 20-25 is satisfactory for the systems considered.) To decide in which of the systems 3, 5, 15, and 39 the PE conformation might be an energy minimum may well turn out to be most difficult on the basis of present knowledge, since the shapes of the energy barriers to internal rotation in ethane (and its derivatives) are not known (cf. Ref. 22). It seems that the balance between torsional strain and bond angle strain close to the PE conformations might well become most delicate, so that the shape of the energy barriers to bond torsion becomes of decisive importance. It should, however, be stressed that no classical mechanical calculations, using methods such as those of Ref. 20-25, have so far been carried out which show that this is so for all of the systems 3, 5, 15, and 39. Indeed, some more general predictions about the strain situations in the all-cis-isomers of all four of these systems can probably be made on the basis of this kind of calculations. This is due to the fact that there are certain limits to the possible shapes of the potential functions for bond torsion. If potential functions with maxima very much sharper or flatter than those

of the functions used in e.g. Ref. 20-25 were utilized, it is easy to realize that experimental data would not be so well reproduced as is often observed. Exactly what these limits could be seems not to have been investigated. In any case, plausible limits certainly can be found and they would perhaps make possible certain predictions as to which of the structures 3, 5, 15, and 39 could have total strain energy minima in the PE conformations and not. Due to the very appreciable uncertainty that would still probably adhere to these predictions and due to the very appreciable mathematical effort involved we have not undertaken any calculations of this kind.

Even in the absence of calculations to support the statement, it would seem to be justified to regard the likelihood of a total strain energy minimum in the PE conformation (or a conformation in which only the nuclear coordinates of the methylene hydrogens are noticeably different from those of the PE conformation) in one or more of the structures 3, 5, 15, and 39 as quite substantial. It also seems quite likely that those of the structures that perhaps do not have total strain energy minima exactly in the conformations indicated, still have such minima quite close to them. (The best way to test these statements would seem to be to prepare and investigate the compounds in question, rather than to carry out calculations.) If this is really so it is expected to give rise to a unique strain situation in the compounds, characterized by total strain energy minima very low in bond angle strain and nongeminal, nonvicinal nonbonded interactions and so high in torsional strain that the latter approaches the maximum possible amount for the number of ethanoid fragments present, a situation that may be expected to not be paralleled in any other kind of organic structures. An attempt to discuss the consequences of this will be made in the following section.

3.5 Discussion of Theoretically Interesting acs-Polyquinanes

The mere knowledge that the likelihood for the strain situations indicated in the last paragraph of section 3.4 is substantial in the case of the all-cis-isomers of the structures 3, 5, 15, and 39 (Scheme IV) should make the preparation

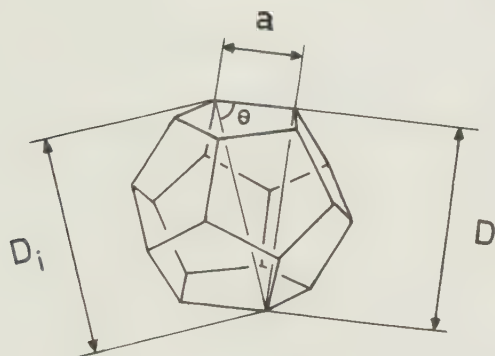
and investigation of these structures of great interest, because if the anticipated strain situations are actually at hand they will make possible a variety of studies of fundamental nature, impossible to carry out on any other kind of structure. As examples may be mentioned studies of the cumulative effects of bond torsion upon carbon hybridization and bridgehead reactivity. (Concerning the dramatic effect of torsional strain upon bridgehead reactivity as revealed in the case of the all-cis-tricyclo[5.2.1.0^{4,10}]dec-10-yl system, see section 4.2.9.) Data from thermochemical studies of the systems could probably be used to advantage in attempts to improve torsional strain potential functions used in classical mechanical calculations of total strain energies of organic molecules, such as those of Ref. 20-25. After the geometries of the conformations of minimum total strain energy of the all-cis-isomers of the structures 3, 5, 15, and 39 were known by X-ray analyses of the compounds themselves or of suitable derivatives, it seems not to be excluded that even the approximate shapes (close to the maxima) of the energy barriers to internal rotation of an ethanoid fragment such as $C_2CH-CHC_2$ could be determined. This is due to the fact that these geometries may be quite strongly dependent on the shapes of the barriers, as outlined in section 3.4. It should be added that it seems not to be excluded that stabilizing and destabilizing interactions between the probably relatively energy-rich C-C σ orbitals of eclipsed ethanoid fragments sufficiently large to be experimentally detectable under favourable circumstances, could occur when several of these fragments are brought close together. (These interactions would be similar to those observed between π orbitals in aromatic and antiaromatic compounds but, of course, probably much weaker due to less efficient overlap.) This effect might be too small to be easily detectable in monocyclic cycloalkanes such as cyclobutane, cyclopentane and cyclohexane, but could well be easier to verify in the all-cis-isomers of the structures 3, 5, 15, and 39. This kind of interactions would show up as deviations in the thermodynamic properties from those predicted on the basis of classical mechanical

models, such as those of Ref. 20-25.

The likelihood for an energy minimum in the PE conformation seems to be particularly large in the case of dodecahedrane, for the reason that there are no nonbonded interactions between in-surface hydrogens in this molecule, and for the reason that the skeletal rigidity (i.e. the steepness of the rise in bond angle strain upon distortions away from the PE conformation) seems to be unusually large. This makes dodecahedrane of particular interest in studies such as those just mentioned as well as in other studies. The dodecahedrane system as a whole also seems to be of quantum mechanical interest²⁸. Earlier investigators have expressed their interest in the dodecahedrane system for several further reasons^{29,30}.

Before terminating this section, the geometrical properties of the PE conformation of dodecahedrane should be briefly summarized. The starting point is the regular dodecahedron, whose geometrical properties of interest in the present connection are summarized in Fig. 1. It is seen that the bond angles are quite close to ideal tetrahedral angles (C-C-H: $(180 - 69.097)^\circ = 110.903^\circ$, C-C-C: 108° ; cf. ideal tetrahedral angle: 109.471°). Assuming a C-C bond length of 1.56 Å (cf. section 3.2) the diameter of a sphere touching the carbon nuclei is 4.37 Å. Assuming further a C-H bond length of 1.09 Å and a hydrogen van der Waals' radius of 1.25 Å, the diameter of a sphere that touches the spheres around the hydrogen nuclei defined by the van der Waals' radii of the hydrogens will be 9.05 Å. Assuming a van der Waals' radius of 1.60 Å for the carbons, the diameter of an inscribed sphere, which touches the spheres around the carbon nuclei defined by the van der Waals' radii of the carbon atoms, will be 1.17 Å. This means that the cavity inside the molecule is large enough to contain a helium atom and possibly a neon atom but probably none of the other rare gas atoms. Utilizing the carbon-hydrogen nonbonded potential function used by Hendrickson²⁰ as a carbon-helium nonbonded potential function (which seems to be a suitable choice; cf. helium and hydrogen nonbonded potential functions given in Ref. 20), the energy of the repulsive interaction between one carbon atom and one helium

atom at an internuclear distance of 2.185 Å is found to be 0.37 kcal·mol⁻¹. The total destabilization of the dodecahedrane-helium inclusion compound due to C-He nonbonded interactions would thus be 7.4 kcal·mol⁻¹. Repeating a similar calculation for the dodecahedrane-neon inclusion compound, utilizing the carbon-carbon nonbonded potential function given by Hendrickson²⁰ as a carbon-neon nonbonded potential function, gives a potential energy of 2.84 kcal·mol⁻¹ for



Edge length:

a

Diameter of a sphere which touches the edges: D

Diameter of the circumscribed sphere:

D_i

$$D = \frac{a}{2} (1 + \sqrt{9 + 4\sqrt{5}}) = a (2.618033985 \pm 0.000000035)$$

$$D_i = \frac{a}{2} \sqrt{14 + 4\sqrt{5} + 2\sqrt{9 + 4\sqrt{5}}} = a (2.80251708 \pm 0.00000003)$$

$$\cos \theta = \frac{a}{D_i} = 0.3568220995 \pm 0.0000000045$$

$$\theta = 69.097^\circ$$

Fig. 1. Some properties of the regular dodecahedron.

one C-Ne interaction at an internuclear distance of 2.185 Å, corresponding to a total destabilization of the dodecahedrane-neon inclusion compound due to carbon-neon nonbonded interactions by 57 kcal·mol⁻¹. As already pointed out in Ref. 1, it seems, however, not to be excluded that the dodecahedrane molecule could contain in a bonded state atoms appreciably larger than the helium atom. In the case of some of the transition metal atoms some overlap between the C-C σ orbitals and the atomic orbitals of the metal could thus possibly take place, so as to obtain a centrosymmetrical structure. (Several other fates of a dodecahedrane-metal inclusion compound - if it could somehow be put together - may, of course, also be visualized, e.g. a transformation into an octahedral triquinacene-metal 2:1 π complex or an insertion of the metal atom into a C-C bond followed by a passage of the atom to the outside of the cage in the inserted, bonded state and perhaps by an extrusion giving empty dodecahedrane and metal, etc.) If it is assumed that the C-C internuclear distances are changed only little from those of empty dodecahedrane in a centrosymmetrical complex of this kind, carbon-metal internuclear distances will be close to those found in the metallocenes and metal carbonyls. For a centrosymmetrical dodecahedrane-metal complex with the C-C internuclear distances 1.56, 1.60 and 1.64 Å the carbon-metal internuclear distances 2.185, 2.24 and 2.30 Å, respectively, may be calculated. This may be compared with carbon-metal internuclear distances in e.g. the following compounds: dibenzene chromium, 2.13 Å³¹; dihydridomolybdenum di(cyclopentadienide)³², 2.22-2.37 Å (mean 2.28 Å); ferrocene³³, 2.40 Å; iron pentacarbonyl³⁴, mean 1.82 Å. Attempts to prepare centrosymmetrical dodecahedrane-metal complexes via triquinacene-metal complexes have so far failed (cf. section 4.2.5), but the question of the stability or instability of the dodecahedrane-metal complexes can, nevertheless, by far not be regarded as settled at the present time.

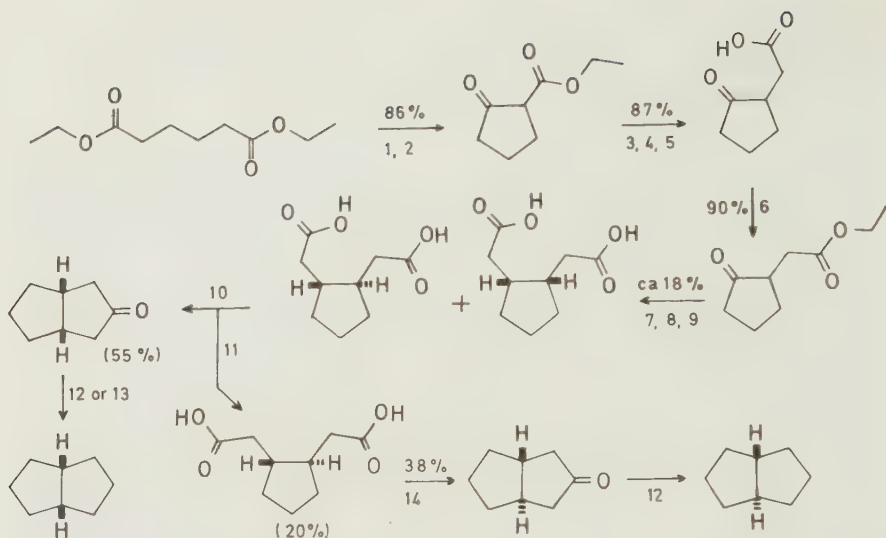
4. Review of Investigations in the Polyquinane Series

4.1 The Simplest Members of the Series

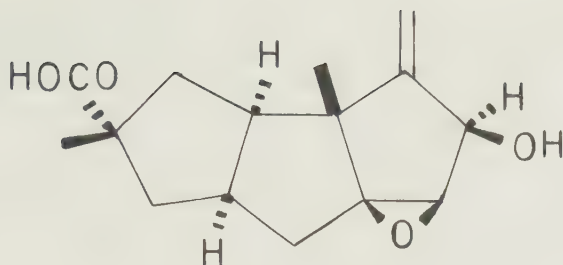
4.1.1 Cyclopentane. A review of the large chemical literature on cyclopentane and its derivatives is considered outside the scope of the present review and will thus not be attempted.

4.1.2 Bicyclo[3.3.0]octane. cis- and trans-Bicyclo[3.3.0]octane were prepared in the 1930:ies by Linstead et al., as shown in Scheme VI³⁵. The heats of combustion of the two compounds were determined shortly afterwards³⁶, and it was found that that of the trans-isomer was larger than that of the cis-isomer by $6.1 \text{ kcal}\cdot\text{mol}^{-1}$ (upon cumbustion as liquids at constant volume). A similar, higher thermodynamic stability of isomers in which all pairs of adjacent bridgehead substituents have a cis-relationship with respect to each other is expected also in all or almost all higher members of the polyquinane series. A review of the literature on derivatives of bicyclo[3.3.0]octane up to 1941 may be found in Ref. 37. Later this field of organic chemistry has grown appreciably. Among relatively easily available derivatives of great potential synthetic interest may be mentioned - besides the monoketones occurring as intermediates in Scheme VI - the 2-monoketone³⁸ and the 2,6-^{39,40}, 3,7-⁴¹ and 2,8-diketones^{42,73,74}. Of outstanding theoretical interest is the stable dilithium pentalenediide⁴³. A preparation of the corresponding uncharged species, pentalene, has on the other hand not succeeded, although hexaphenylpentalene is known. (For a review of the literature on the pentalene problem, see Ref. 44.)

4.1.3 Tricyclo[6.3.0.0^{2,6}]undecane. The carbon skeleton of tricyclo[6.3.0.0^{2,6}]undecane is found in certain fungal metabolites, i.e. hirsutic acid (V)⁴⁵ and the coriolsins⁴⁶. The remaining derivatives of this hydrocarbon known to date have arisen in studies of the synthesis of hirsutic acid⁴⁷ and in studies of the reductive dimerization of 1-acetylcyclopentene



Scheme VI. Synthesis of cis- and trans-bicyclo[3.3.0]octane, by Linstead et al.³⁵. Reagents: 1. Na-C₆H₆; 2. H⁺; 3. Na-petroleum ether; 4. ClCH₂CO₂Et; 5. Hydrochloric acid, reflux; 6. EtOH-HCl; 7. NCCH₂CO₂Et, piperidine; 8. Al-Hg-H₂O-Et₂O; 9. Concentrated hydrochloric acid, reflux; 10. Heat mixture of stereoisomeric acids with Ba(OH)₂ at 280°, recover cis-ketone from distillate; 11. Acidify distillation residue; 12. Clemmensen reduction; 13. Wolff-Kishner reduction; 14. Ba(OH)₂, 340-350°.



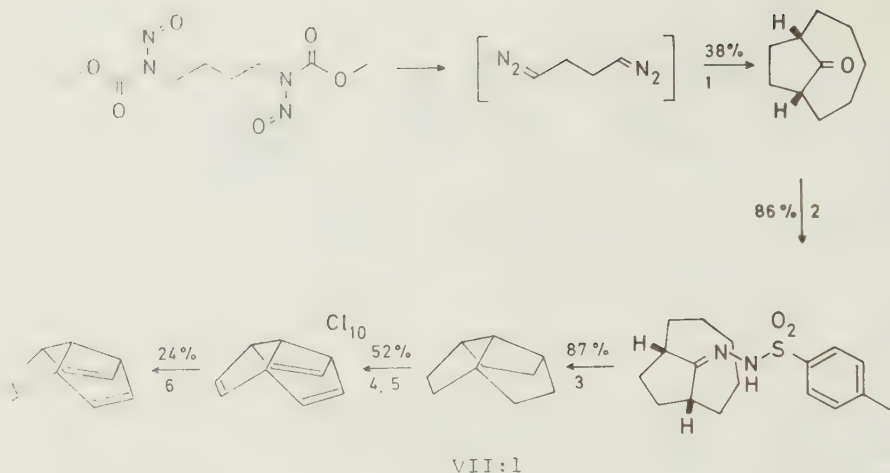
v

and its derivatives⁴⁸. The synthesis of the parent hydrocarbon - probably a relatively trivial synthetic problem - still remains to be carried out.

4.2 Tricyclo[5.2.1.0^{4,10}]decane

4.2.1 The parent hydrocarbon. all-cis-Tricyclo[5.2.1.0^{4,10}]decane (VII:1) was described in 1967 by Jacobson¹ as a product of the sequence of reactions shown in Scheme VII. The structure and stereochemistry of the hydrocarbon follows from the fact that it is also formed upon hydrogenation of triquinacene⁴, i.e. all-cis-tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene. The reverse transformation, i.e. of all-cis-tricyclo[5.2.1.0^{4,10}]decane into triquinacene, may also be accomplished in good yield, as shown in Scheme VII^{2,3}, but this transformation proves in principle nothing definite about the structural and stereochemical interrelationship of the two compounds, since reaction conditions are used which could possibly bring about rearrangements (cf. Ref. 2). The structure of triquinacene again follows immediately as a trivial consequence of a consideration of little more than its molecular formula, NMR spectrum and UV spectrum (cf. Ref. 49, 4).

The carbenoid thermal decomposition of the sodium salt of the tosylhydrazone of cyclooctanone gives rise to cis-cyclooctene, cis-bicyclo[5.1.0]octane and cis-bicyclo[3.3.0]octane all in appreciable quantities⁵⁰, whereas a similar reaction in



Scheme VII. Synthesis of triquinacene, by Jacobson^{1,2,3,4}.

Reagents: 1. $\text{K}_2\text{CO}_3\text{-CH}_3\text{OH-CHCl}_3\text{-cyclohexanone}$; 2. $\text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_2\cdot\frac{1}{2}\text{H}_3\text{-EtOH-HCl}$; 3. $\text{NaNHCOCH}_3\text{-CH}_3\text{CONH}_2$, $135\text{-}175^\circ$; 4. $\text{Cl}_2\text{-CCl}_4\text{-hv}$; 5. $\text{I}_2\text{-C}_2\text{Cl}_6$, 260° , 24 h; 6. $\text{Li-t-BuOH-THF-H}_2\text{O}$.

The cyclopentanone case gives cyclopentene only⁵⁰. Since the bicyclo[5.2.1]decane system has shown to be flexible enough that e.g. deuteration of 10-ketobicyclo[5.2.1]decane by enolization is possible⁵², it could seem justified in a preliminary attempt to predict the behaviour of 10-carbenabicyclo[5.2.1]decane to assume that the conformational situations in the five- and eight-membered rings of this carbene were similar to those in the simple monocyclic carbenes just mentioned. The prediction would be that the thermal, carbenoid decomposition of the sodium salt of 10-ketobicyclo[5.2.1]decane would give rise to bicyclo[5.2.1]dec-1(10)-ene, all-cis-tricyclo[5.3.0.0^{2,10}]decane, and all-cis-tricyclo[5.2.1.0^{4,10}]-

decane. A closer study of the mechanical properties of the bicyclo[5.2.1]decane system with the aid of molecular models, however, suggests that the five-membered ring puts severe restrictions upon the conformational mobility of the eight-membered ring, as compared to the case of cyclooctane, in such a way as to favour 1,5-insertion over 1,2- and 1,3-insertion in the 10-carbena derivative. This expectation has been confirmed by experiments which show that the specificity of 1,5-insertion is indeed very appreciably improved on going from carbenacyclooctane to 10-carbenabicyclo[5.2.1]decane^{1,4}.

NMR studies⁴ have also shown that for both 10-ketobicyclo[5.2.1]decane and its tosylhydrazone a large fraction of the molecular population is likely to exist in the neighbourhood of a conformation in which the eight-membered ring has an adamantoid saddle arrangement. This may be taken as a further experimental confirmation of the above-mentioned predictions made on the basis of studies of molecular models.

For further syntheses which amount to the build up of the carbon skeleton of tricyclo[5.2.1.0^{4,10}]decane, see sections 4.2.2, 4.2.4, and 4.2.6.

4.2.2 Monofunctional Derivatives. The four possible methylurethanes derived from all-cis-tricyclo[5.2.1.0^{4,10}]decane have been obtained by Paquette et al.⁵³ from the hydrocarbon by reaction with methoxycarbonylnitrene generated by thermal decomposition of methyl azidoformate. From the behaviour of methoxycarbonylnitrene in other systems, which suggests that the carbon atom directly involved in the transition state to nitrene insertion has free radical character, and from the observed product ratio, the authors conclude that the relative free radical reactivities at the different positions of all-cis-tricyclo[5.2.1.0^{4,10}]decane are probably normal and suggesting that the hydrocarbon is relatively strain-free. In the same paper⁵³ the oxidation of the hydrocarbon by chromyl acetate is also described. It is found to give the expected products, except that no derivatives with a substituent at position 10 are observed, an indication that C(10) is poor in supporting positive charge. That the solvolysis rate of 10-

-tosyloxytricyclo[5.2.1.0^{4,10}]decane is indeed exceptionally low has later been demonstrated by von R. Schleyer et al.⁷¹ (cf. section 4.2.9). 10-Hydroxy-all-cis-tricyclo[5.2.1.0^{4,10}]-decane, the only hydroxy derivative not obtainable from the corresponding hydrocarbon by the procedures of Ref. 53, has been prepared by Gutsche et al. by reductive cyclization of 4-exo-tosyloxybicyclo[5.2.1]decan-10-one⁵⁴.

4.2.3 Polychlorination. Forcing photochlorination of all-cis-tricyclo[5.2.1.0^{4,10}]decane has been found by Jacobson² to give rise to mixtures typically containing four dominant constituents, i.e. 10-H-nonachloro-all-cis-tricyclo[5.2.1.0^{4,10}]-deca-2,5,8-triene (NCT), perchloro-all-cis-tricyclo[5.2.1.0^{4,10}]-deca-2,5,8-triene (PCT), 10-H-undecachloro-all-cis-tricyclo[5.2.1.0^{4,10}]deca-2,5-diene (UCTD), and perchloro-all-cis-tricyclo[5.2.1.0^{4,10}]deca-2,5-diene (PCTD). The products may be converted in high yield into pure PCT in a thermal chlorination-dechlorination process by heating with iodine and hexachloroethane². Pure NCT may be obtained from the products by catalytic hydrogenation². Pure UCTD and PCTD, finally, may be obtained from pure NCT and pure PCT by photochlorination². The identity of NCT and PCT as derivatives of tricyclo[5.2.1.0^{4,10}]-deca-2,5,8-triene follows from the convertibility of NCT into PCT², of PCT into NCT (cf. Ref. 6, Experimental), and of NCT and/or PCT into 1,2,3,5,6,8,9-heptachloro-all-cis-tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene⁵, 2,3,5,6,8,9-hexachloro-all-cis-tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene³ and triquinacene³ and from the ultraviolet spectra which show that conjugation is absent². That the stereochemistry of PCT is that which is most stable, i.e. most likely all-cis, follows from the fact that the compound is stable under a variety of very forcing reaction conditions (such as prolonged heating to 260-320° at atmospheric pressure), expected to bring about equilibration of stereoisomers². (For some further discussion of why equilibration of stereoisomers is likely to be possible under the forcing reaction conditions described in Ref. 2, see section 1C in Ref. 6.) The structure of PCT as the all-cis-2,5,8-triene was later confirmed by single crystal X-ray diffraction

studies⁵⁵. Also the structure of NCT may be regarded to be established beyond reasonable doubt².

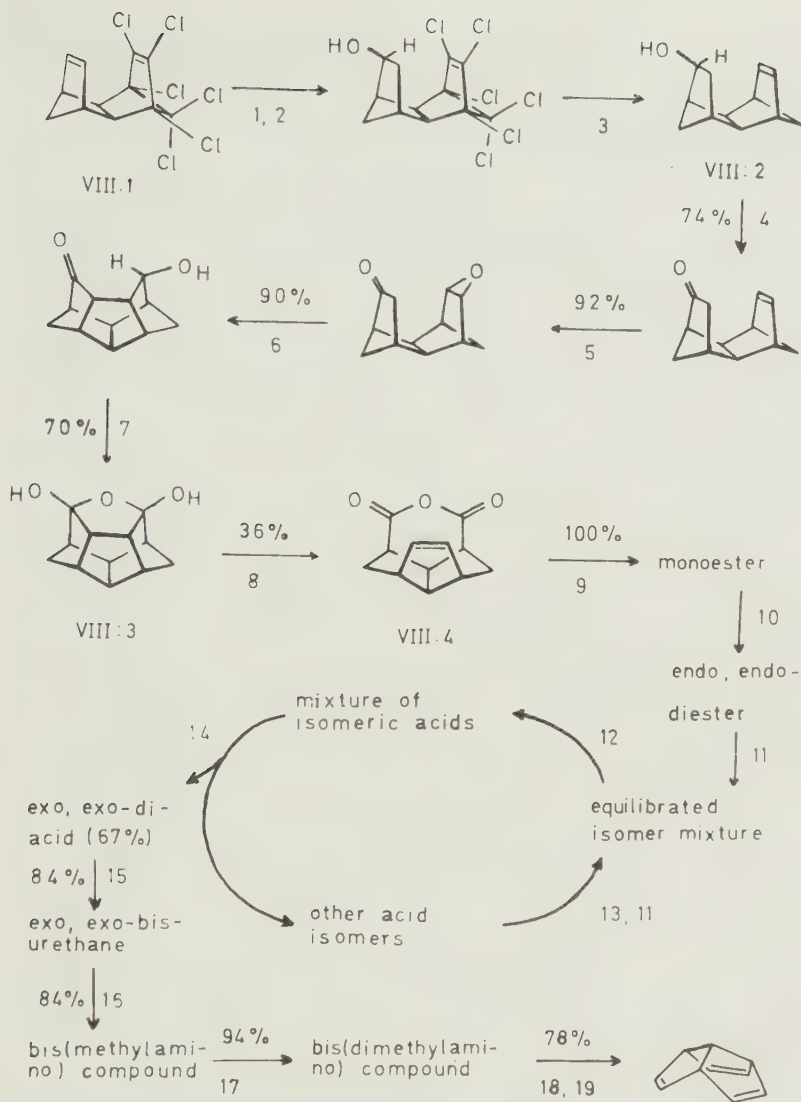
The detailed molecular geometry of PCT as revealed by the X-ray analysis⁵⁵ is highly interesting. It is found to be very close to C_{3v} symmetry with perfectly eclipsing chlorines at the bridgeheads. Furthermore, the C(10)-Cl(10) bond is unusually short, with a length intermediate between those typically found for olefinic and aliphatic C-Cl bonds⁵⁵, despite the fact that the three adjacent allylic, eclipsing chlorines probably will tend to force Cl(10) outwards (so as to stretch the C(10)-Cl(10) bond). This may possibly indicate that the torsional arrangement of C-C bonds at C(10) in PCT influences the hybridization of this carbon atom so as to increase the percent of s-character in the carbon orbital that participates in the C(10)-Cl(10) bond. A similar effect of the torsional arrangement at C(10) also in saturated derivatives of all-cis-tricyclo[5.2.1.0^{4,10}]-decane could possibly explain the exceptional solvolytic reactivity of such derivatives with a substituent at position 10 (see section 4.2.9). Further studies of this problem, in particular a determination of ^{13}C - 1H coupling constants (cf. Ref. 57) in suitable derivatives of all-cis-tricyclo[5.2.1.0^{4,10}]-decane, would seem to be of great interest.

As already mentioned, PCT is thermally highly stable. It may thus be passed as a gas (1 atm) through a glass tube heated at 450° with only little change provided that contact times are kept relatively short. More prolonged heating to temperatures as high as 450° leads to carbonization and formation of chlorine. Gas phase pyrolysis at 650° and atmospheric pressure with short contact times leads to excellent yields of octachloronaphthalene, provided that the walls of the pyrolysis tube are basic (cf. Ref. 2). In a pyrolysis tube with walls of an acidic material, such as quartz, a similar pyrolysis gives mostly only rather little octachloronaphthalene, but instead appreciable quantities of a chlorocarbon with the molecular formula $C_{18}Cl_{12}$. The same chlorocarbon may also be obtained by heating a mixture of PCT and aluminium chloride or a mixture of octachloronaphthalene, hexachloroethane (chlorinating agent) and aluminium chloride to 260° for 48 hours (cf. Ref. 2). It

seems most likely that octachloroindene, formed in acid catalyzed ring-contracting chlorinations from octachloronaphthalene (cf. Ref. 56), is the crucial intermediate in all three of the above processes of formation of the chlorocarbon $C_{18}Cl_{12}$.

4.2.4 Syntheses of Triquinacene. Triquinacene, i.e. all-cis-tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene was first obtained in 1964 by Woodward and coworkers by the sequence shown in Scheme VIII^{49,58}. The starting material is the Diels-Alder adduct between 1,2,3,4,7,7-hexachlorobicyclo[2.2.1]heptadiene and cyclopentadiene, VIII:1 (isodrin), which may be converted to the alcohol VIII:2 by a procedure due to Winstein et al.⁵⁹. Oxidation, epoxidation, transannular cyclization and oxidation converted the alcohol into the interesting stable diketone hydrate VIII:3. The cage VIII:3 was next opened, with the formation of the anhydride VIII:4 by oxidation with lead tetraacetate. The conditions used in this step are reminiscent of those in the oxidative decarboxylation due to von E. Doering et al.⁶⁰. After esterification of VIII:4, base-catalyzed equilibration of stereoisomers, hydrolysis of the equilibrated ester mixture and crystallization of the mixture of stereoisomeric acids from chloroform, the pure exo,exo-diacid corresponding to VIII:4 was obtained. The other stereoisomeric acids could be recycled for recovery of more exo,exo-diacid⁴⁹ (cf. Scheme VIII). The exo,exo-diacid was subjected to Curtius degradation, giving an exo,exo-bisurethane. The latter was reduced by lithium aluminium hydride followed by the Wallach methylation procedure, giving a bis(dimethylamino) compound. Conversion of the diamine into the bisamine oxide and pyrolysis gave triquinacene.

The synthesis of triquinacene next to be described is that due to Jacobson (1967)¹. This synthesis has later been appreciably improved^{2,3,4} and would now constitute the method of choice for the preparation of the hydrocarbon. The sequence of reactions used is shown in Scheme VII. (Certain improvements of the procedure not found in Ref. 1 have been included in Scheme VII.) For some comments on the reaction used to obtain the hydrocarbon VII:1 in this sequence, see section 4.2.1;



Scheme VIII. Synthesis of triquinacene, by Woodward et al.⁴⁹
 Reagents: 1. B_2H_6 ; 2. H_2O_2 ; 3. $Li-t-BuOH-THF$; 4. $CrO_3-C_5H_5N$;
 5. $CH_3CO_3H-CH_3CO_2H-CH_2Cl_2-NaO_2CCH_3$; 6. $KO-t-Bu-Et_2O-THF$;
 7. $CrO_3-H_2O-Et_2O$; 8. $Pb(OAc)_4-C_6H_6$, reflux; 9. CH_3OH ; 10. CH_2N_2 ;
 11. $NaOCH_3-CH_3OH$; 12. $NaOH-H_2O-CH_3OH$; 13. esterification;
 14. crystallization from $CHCl_3$; 15. Curtius degradation;
 16. $LiAlH_4$; 17. $HCHO-HCO_2H-H_2O$; 18. H_2O_2 ; 19. $125-140^\circ/10-30$
 mmHg.

for comments on the chlorination of the hydrocarbon VII:1, see section 4.2.3. The dechlorination of PCT to triquinacene has been carried out by two different routes, either directly or via 2,3,5,6,8,9-hexachloro-all-cis-tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene (HCT) as an intermediate³. In the studies of the preparation of HCT a further partially dechlorinated PCT of potential synthetic interest was isolated, i.e. 1,2,3,5,6,8,9-heptachloro-all-cis-tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene (HpCT)⁵. HCT and HpCT were both obtained as products of the reaction between PCT and a modified hydridoaluminate reagent obtained from the reaction between LiAlH_4 and water at low temperature^{3,5}. (LiAlH_4 itself is unsatisfactory.) The structures of the compounds follow immediately from the NMR spectra, which are of the AB_3 and AB_2 types, and from the ultraviolet spectra, which show that conjugation is absent^{3,5}. The dechlorination of PCT to HCT is likely to occur with complete retention of configuration at the bridgeheads substituted, because NCT (see section 4.2.3), when dechlorinated under the same conditions as PCT, also gives a high yield of HCT³. Though it cannot be excluded at present that the hydridoaluminate reagent used actually favours substitution with retention of configuration in a substrate where both inversion and retention are possible (cf. Ref. 3), it would seem that substitution with retention of configuration is actually the normal stereochemical course of a substitution reaction at a bridgehead in a derivative of all-cis-tricyclo[5.2.1.0^{4,10}]decane, because inversion would be strongly disfavoured due to strain. Complete dechlorination of PCT and HCT to triquinacene was achieved by a mixture of lithium, tertiary butanol and tetrahydrofuran³.

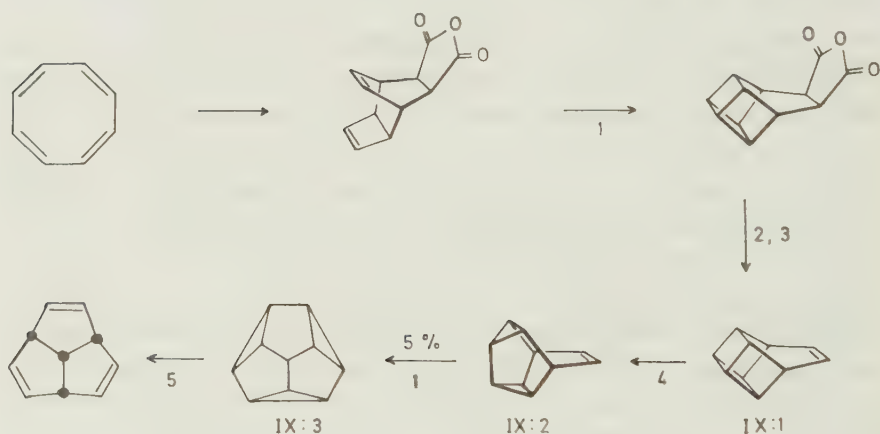
Interestingly certain amounts of water must be added to the reaction mixture in order to obtain triquinacene³. The function of the water is presumably to keep the basicity of the reaction mixture relatively low, because LiO-t-Bu is easily soluble in the reaction mixture, whereas LiOH is not. It has further been found that the chlorinated substrates are resinified by strongly basic media. It seems reasonable to assume that this is also true for partially dechlorinated intermediates formed from the substrates. Apparently, when the basic constituents of the reaction mixture are present almost entirely as a solid LiOH sludge (due to the addition of

water) base-dependent resinification reactions either must occur as homogeneous reactions at quite low base concentrations and so will be slow, or alternatively must occur as heterogeneous reactions which may well also be comparatively slow. In the absence of added water, high concentrations of dissolved LiO-t-Bu will be present, which is expected to lead to rapid resinification. However, the concentration of water must not be too high, because then only unreacted starting material and no triquinacene is obtained³. It now seems most probable that under optimum conditions for dechlorination a concentration gradient is set up close to the lithium surface such that LiO-t-Bu but no water exists in the solution close to the surface, whereas free water but no LiO-t-Bu exists in the bulk of the solution. Under these circumstances the availability of protons close to the lithium surface may be low enough that efficient dechlorination occurs there. Of course, resinification reactions will also occur close to the lithium surface due to the strongly basic medium present there, but competition between resinification reactions and dechlorination may be in favour of dechlorination as long as the basic zone is narrow. In the bulk of the solution, on the other hand, basicity will be low and free water will be present so that resinification becomes slow there. (In the absence of added water the basicity of the bulk of the solution would be high, but dechlorination would still be slow there, which means that resinification reactions could successfully compete with the dechlorination.)

A third synthesis which amounts to a preparation of triquinacene has recently been preliminarily reported⁶¹. A possible complete sequence from commonly available starting materials is outlined in Scheme IX. IX:1, obtainable from cyclooctatetraene as shown^{63,64}, rearranges to IX:2 under the catalytic influence of silver ions⁶². The order of the reactions leading to IX:2 may, however, also be changed⁶². IX:2, upon ultraviolet irradiation, gives among other products the highly interesting triply cyclopropanoid valence tautomer of triquinacene, IX:3, possible to isolate in a 5 % yield⁶¹. IX:3 is thermodynamically unstable and rearranges in a thermally symmetry allowed reaction to triquinacene. The half-life of IX:3 at 90° is ca 60 min⁶¹.

4.2.5 Investigations of Triquinacene. As outlined briefly in the introduction to Ref. 1, triquinacene is interesting for at least two reasons, i.e. on the one hand as a potential

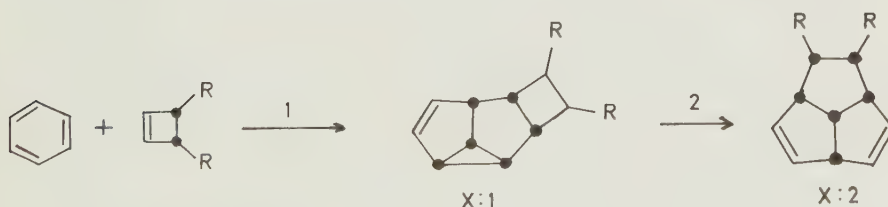
monomer capable of yielding dodecahedrane upon dimerization, and on the other hand as a structure of potential utility in the preparation of certain theoretically interesting octahedral transition metal complexes of the general formula T_2M , T = triquinacene, M = metal atom. So far little progress has been made in either field of investigation, in the author's laboratory or elsewhere. All attempts to dimerize triquinacene to dodecahedrane (or to a precursor capable of yielding dodecahedrane upon further cyclization) have thus failed so far. Also attempts to prepare complexes T_2M have hitherto failed, although certain other complexes of triquinacene have been isolated (I.T. Jacobson, unpublished). Owing to the great number of experimental possibilities, neither field can, however, be regarded as exhausted of possibilities at present.



Scheme IX. Synthesis of hexacyclo[4.4.0.0.^{2,4}0.^{3,9}0.^{5,7}0.^{8,10}]-decane and triquinacene⁶¹⁻⁶⁴. Reagents: 1. $h\nu$; 2. H_2O ; 3. $Pb(OAc)_4-C_5H_5N$; 4. Ag^+ ; 5. heat.

4.2.6 Further Syntheses of Derivatives of Tricyclo[5.2.1.0^{4,10}]-deca-
decane. A most interesting synthesis of all-cis-tricyclo-
[5.2.1.0^{4,10}]deca-2,5-diene, X:2 (R = H), has been found by
Srinivasan⁶⁵ (see Scheme X). Benzene is added photochemically
to cyclobutene, giving X:1 (R = H) as a major product (yield
20-60 %). X:1 (R = H) upon pyrolysis gives X:2 (R = H) (yield
50 %). The skeletal structure and stereochemistry of the product
follows from its hydrogenation⁶⁵ to material identical with
saturated hydrocarbon prepared according to Ref. 1. The stereo-
electronic courses of the photochemical and pyrolytic reactions
have been shown to be as indicated in Scheme X by studies of
corresponding reactions between hexadeuterobenzene and cyclo-
butene⁶⁵, between benzene and cis-3,4-dimethylcyclobutene⁶⁶,
and between hexadeuterobenzene and cis-3,4-dimethylcyclo-
butene⁶⁶, which gave derivatives labeled in agreement with
Scheme X. Also the corresponding reactions between toluene and
the dimethylbenzenes and cyclobutene have been studied⁶⁷.
Particularly interesting from the viewpoint of the present
review is the application of the reaction to the synthesis of
a higher member of the polyquinane series; see section 4.3.2.

A preliminary report⁶⁸ has been given of a transformation
of a dimer of cyclopentadienecarboxylic acid (Thiele's acid) by
a fourteen step route into 8-keto-all-cis-tricyclo[5.2.1.0^{4,10}]-
deca-2,5-diene, identical with material prepared by a seemingly
much easier route^{68,69} from triquinacene.

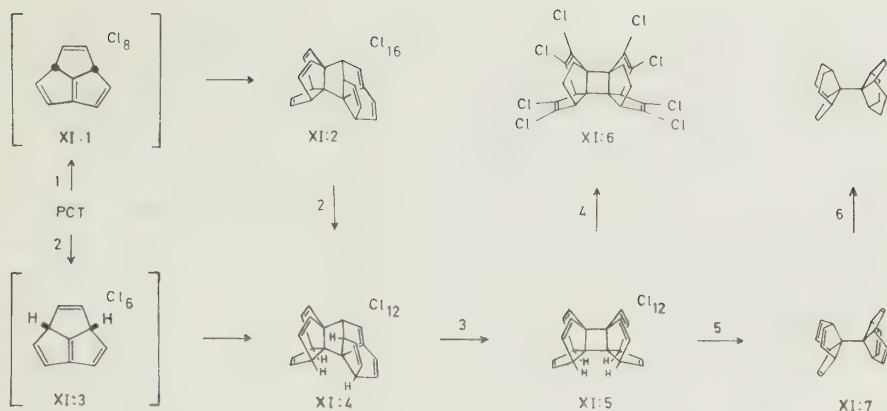


Scheme X. Synthesis of all-cis-tricyclo[5.2.1.0^{4,10}]deca-2,5-
diene and its derivatives by Srinivasan^{65,66}. Reagents:
1. $h\nu$; 2. heat.

4.2.7 Tetraenic Elimination Products of Chlorinated Derivatives of Triquinacene. Perchloro-all-cis-tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene (PCT), upon mild catalytic hydrogenation⁶, gives rise to the dimer XI:2, i.e. a dimer of perchloro-cis-tricyclo[5.2.1.0^{4,10}]deca-1(10),2,5,8-tetraene (XI:1). Upon treatment instead with zinc powder in tetrahydrofuran-ethanol, PCT gives a dodecachloro analogue of XI:2, i.e. XI:4⁶. The structural proofs for XI:2 and XI:4 depend upon the convertibility of XI:2 into XI:4⁶ (cf. Scheme XI) and spectroscopic studies⁶. XI:2 and XI:4, when heated to ca 200^o, exist in chemical equilibrium with the monomers XI:1 and XI:3⁶. For example, a carbon tetrachloride solution of XI:2 containing ethylene, after being heated briefly to 210^o, yields the Diels-Alder adduct between XI:1 and ethylene⁶.

The monomers XI:1 and XI:3 dimerize essentially instantaneously to the dimers XI:2 and XI:4 even at room temperature, as found from the behaviour of the dimers upon monomerization-redimerization experiments in an evacuated sublimation apparatus⁶. This behaviour, taken in conjunction with the structures XI:2 and XI:4 deduced for the dimers, is interesting, since it demonstrates that a double bond between carbons 1 and 10 in a derivative of tricyclo[5.2.1.0^{4,10}]decane can be (and probably always is) quite reactive. This difference as compared to a more ordinary, tetraalkyl substituted double bond (which would as a rule not give rise to Diels-Alder adducts even with quite reactive dienes) is not quite unexpected, because the skeletal framework of the tricyclo[5.2.1.0^{4,10}]decane system will tend to force the six carbon nuclei closest to the π orbital of the 1(10) double bond out of coplanarity. A similar high reactivity of a tetraalkyl substituted double bond is to be expected in other members of the polyquinane series whenever the double bond is situated in a peri-fusion.

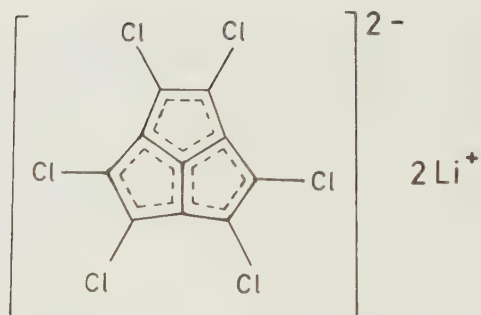
XI:4, when heated briefly to 280^o, rearranges to the more stable cyclobutanoid isomer XI:5⁷. Upon hydrogenation, XI:5 in a somewhat unusual reaction, gives XI:6⁷. An explanation of this behaviour as due to the formation of a reactive intermediate from XI:5 by a Cope rearrangement has been given⁷. The behaviour of XI:5 upon dechlorination by lithium and



Scheme XI. Transformation of perchloro-all-cis-tricyclo-[5.2.1.0^{4,10}]deca-2,5,8-triene (PCT) into dimeric compounds^{6,7}. Reagents: 1. Pd-H₂-THF, 65°; 2. Zn-EtOH-THF, 65°; 3. 280-290°, 10 min.; 4. Pd-H₂-HOAc, 118°; 5. Li-t-BuOH-THF; 6. Pd-H₂-EtOH.

tertiary butanol in tetrahydrofuran has also been investigated⁷. Under these circumstances the cyclobutane ring of XI:5 is opened specifically so as to introduce two new allylic hydrogens, giving the interesting species XI:7 (cf. Scheme XI).

4.2.8 Dilithium hexachloroacepentylendiide (VI). The reaction between PCT and excess butyl lithium in a hydrocarbon solvent at - 70° gives rise to dilithium hexachloroacepentylendiide (VI) as a prominent product⁸. The demonstration of the formation of this dianion so far relies mainly upon the fact that its cold solution, when quenched with a cold solution of hydrogen chloride in an alcohol ROH, gives rise to a product containing a compound C₁₀H₄Cl₆(OR)₂ as the principal constituent⁸. Little is known about the chemistry of the dianion so far.



VI

4.2.9 Solvolysis of all-cis-Tricyclo[5.2.1.0^{4,10}]dec-10-yl tosylate. Studies of the bridgehead reactivities in derivatives of acs-polyquinanes, in particular the all-cis-isomers of the hydrocarbons 3, 5, 15, and 39 (Scheme IV), are of appreciable theoretical interest (cf. section 3). Such studies have already been carried out in the case of 10-substituted derivatives of all-cis-tricyclo[5.2.1.0^{4,10}]decane by von R. Schleyer and coworkers^{70,71}. The result may be expressed in the form that on solvolysis under the same conditions, the rate of solvolysis will decrease by a factor of ca $3 \cdot 10^{-6}$ on going from a 1-adamantyl derivative to an all-cis-tricyclo[5.2.1.0^{4,10}]dec-10-yl derivative with the same leaving group. In Ref. 71 ΔH of formation of carbenium ions from the substrates investigated are estimated, based on classical-mechanical, semiempirical calculations of total strain energies. An excellent correlation with experimentally observed rates of solvolysis, varying by more than eighteen powers of ten, is obtained, with one notable exception - the all-cis-tricyclo[5.2.1.0^{4,10}]dec-10-yl system. This system is found experimentally to solvolyse at a rate ca 10^9 times slower than predicted on the basis of the calculations. The authors propose

that an electronic effect not taken into account by the calculations and brought to light by the unique geometry of the all-cis-tricyclo[5.2.1.0^{4,10}]decane system should be assumed to be the origin of the discrepancy, and suggest that the degree of stabilization of a nonplanar carbenium ion depends upon the dihedral angles between the substituents on the charged carbon atom and the substituents on an adjacent carbon atom in such a way that maximum stabilization is obtained when the most stabilizing substituent on the adjacent carbon atom is trans-staggered with respect to the vacant orbital of the carbenium ion. Further studies would seem to be needed, however, before it can be claimed that this new effect is well understood. Among other things, studies of the state of hybridization of C(10) in all-cis-tricyclo[5.2.1.0^{4,10}]decane and its derivatives (cf. section 4.2.3), a direct determination of the preferred conformation of a 10-substituted derivative by X-ray analysis, and thermochemical studies of the hydrocarbon would seem to be desirable.

4.3 Higher Members of the Series

4.3.1 Tetracyclo[6.6.0.0^{2,6}.0^{10,14}]tetradecane. Derivatives of the all-cis,all-syn-isomer of tetracyclo[6.6.0.0^{2,6}.0^{10,14}]-tetradecane (formula 7 in Scheme IV) are intermediates in the recently reported synthesis of the peristylane system; see section 4.3.4.

4.3.2 Tetracyclo[5.5.1.0^{2,6}.0^{10,13}]tridecane. A derivative of the all-cis-syn-isomer of tetracyclo[5.5.1.0^{2,6}.0^{10,13}]tridecane (formula 6 in Scheme IV) has been prepared by an application of Srinivasans photochemical-thermal synthesis of derivatives of tricyclo[5.2.1.0^{4,10}]decane to the case of the reactants benzene and bicyclo[3.2.0]hepta-2,6-diene⁶⁶. It would be most interesting to investigate whether this elegant approach to polyquinanes with acs-stereochemistry could possibly be extended to still higher members of the polyquinane series, such as e.g. 19 in Scheme IV by reacting benzene with the hydrocarbon VII (which has hitherto not been prepared). Actually, C₁₈-hexaquinacene

(Scheme V) could well arise directly in small amounts by simply irradiating benzene alone followed by a heat treatment, by double addition of benzene to Dewar benzene (which forms upon irradiation of benzene⁷²).



VII

4.3.3 Pentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradecane. A derivative of the all-cis-isomer of pentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradecane (formula 9 in Scheme IV) is an intermediate in the reported synthesis of the peristylane system; see section 4.3.4.

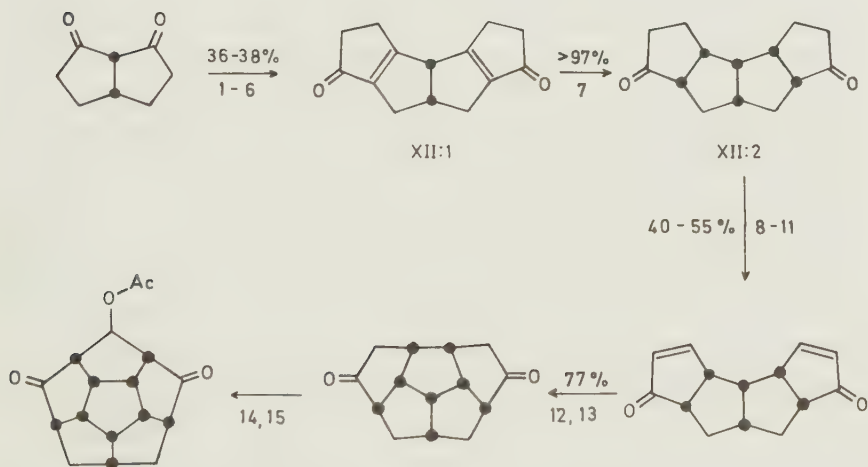
4.3.4 Hexacyclo[7.5.1.0^{3,13}.0^{5,12}.0^{7,11}.0^{10,14}]pentadecane. Eaton et al. recently published a report of the synthesis of a derivative of hexacyclo[7.5.1.0^{3,13}.0^{5,12}.0^{7,11}.0^{10,14}]pentadecane (peristylane; formula 15 in Scheme IV)⁷³. The sequence used is summarized in Scheme XII. The starting material used is cis-bicyclo[3.3.0]octa-2,8-dione, a previously known compound⁴² whose preparation has been improved^{73,74}. Annellation with two five-membered rings as shown gave the bisenone XII:1. Hydrogenation of the latter occurred stereospecifically from the least hindered side, giving the all-cis,all-syn-diketone XII:2. Introduction of unsaturation in the diketone XII:2, reductive cyclization and a condensation with ethyl formate completed the build-up

of the peristylane system.

5. Summary

1. A definition of the polyquinane concept based upon graph theory has been given.

2. Theoretical predictions as well as experimental observations on polyquinanes so far known suggest that these compounds - and in particular the acs-polyquinanes (defined in the text) - will be similar to each other in many respects and sufficiently different from other organic compounds that a class-name is justified.



Scheme XII. Synthesis of the peristylane system by Eaton et al.⁷³. Reagents: 1. $\text{Li}(\text{CH}_2)_3\text{OCH}(\text{CH}_3)\text{OC}_2\text{H}_5$; 2. $(\text{NH}_4)_2\text{SO}_4\text{-H}_2\text{O}$; 3. repeat step 1; 4. H^+ , H_2O ; 5. $\text{CrO}_3\text{-H}^+\text{-H}_2\text{O}$; 6. $\text{P}_4\text{O}_{10}\text{-CH}_3\text{SO}_3\text{H}$; 7. $\text{Pd-H}_2\text{-EtOAc}$, -20° ; 8. $\text{HOCH}_2\text{CH}_2\text{OH}$, H^+ ; 9. pyridinium bromide-perbromide-THF, -10 to 0° ; 10. $\text{NaOCH}_3\text{-Me}_2\text{SO}$, 95° ; 11. $\text{H}_2\text{O-H}^+$; 12. $h\nu$; 13. $\text{Zn-CH}_3\text{CO}_2\text{H}$, reflux; 14. $\text{HCO}_2\text{Et-KO-t-Bu}$; 15. acetylation.

3. A qualitative discussion of the strain situation in the acs-polyquinanes in terms of presently commonly used classical mechanical models of hydrocarbon total strain has been given, which indicates that the strain situation in certain members of the series should be unique and might lead to theoretically important discoveries after the respective compounds have become synthetically available.

4. A review of investigations so far made in the field of the polyquinanes has been given, which shows that preparative progress has been rapid during the last few years and that certain theoretically interesting results have recently been obtained.

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